

# CATALYTIC DEGRADATION OF HIGH DENSITY POLYETHYLENE AND WASTE PLASTIC BELOW 200 °C

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## Introduction

High density polyethylene (HDPE) is the dominant component of several major waste plastic streams. Furthermore, under thermally as well as catalytically controlled degradation conditions, HDPE is clearly an excellent potential source of hydrocarbon products. Unfortunately, HDPE is notoriously resistant against thermal degradation, requiring pyrolysis temperatures well above 400°C in order to exhibit sufficiently high degradation rates[1]. These high temperatures lead to loss of selectivity, increased secondary reactions, coke formation and reduced catalyst life. Although Wender et al. reported catalytic scission of polymethylene bonds at temperatures as low as 160°C in short chain paraffinic compounds such as hexadecane[2], few authors have reported successful catalytic conversion of HDPE below 300 °C. The two main obstacles encountered appear to be the limited mobility of long chain molecules even in the molten stage and poor hydrogen ( $H_2$ ) diffusion, thus leading to transport-limited interactions between catalytic sites and potential bond scission sites. Also the frequent presence of organic and inorganic moieties other than HDPE that negatively affect catalyst performance, e.g. through catalyst deactivation ("fouling") poses a formidable obstacle against successful catalytic conversions of waste plastic. Attempts to reduce transport limitations for long chain HDPE molecules have included use of very high catalyst loadings[3], or improved mixing and blending techniques for catalyst and polymer e.g. by means of cryogenic milling[4] or through solvent blending[3].

The present research was concerned with a systematic investigation of the catalytic degradation of HDPE polymers at low temperature under  $H_2$  pressure, using finely dispersed superacid catalysts, i.e.  $Pt/ZrO_2/SO_4$ . A Calu model 151 high pressure thermogravimetry (HPTG) system with specially constructed on-line gas chromatography/mass spectrometry (GC/MS module) capable of recording temperature programmed GC/MS profiles at 90 second intervals provides detailed kinetic (rates, yields) and mechanistic (product identity) information from a single HPTG run.

## Experimental

**Materials.** Four different HDPE samples were studied: (1) a pure HDPE (den., 0.96g/cm<sup>3</sup>; average MW, 250,000; Tm, 135 °C) provided by HTI and originally manufactured by Solvay polymers; (2) a pure HDPE (den., 0.959 g/cm<sup>3</sup>; average MW, 125,000; Tm, 130°C) obtained from Aldrich Chemical Co.; (3) a HDPE-rich commingled waste plastic sample (primarily HDPE with 5-10% polypropylene, 3-5% polystyrene and 1-2% inorganic fillers plus organic colorizing agents) provided by the American Plastics Council (APC) and included in the University of Utah Waste Materials Sample Bank; (4) a cleaned milk bottle without its cap and label.

**Catalysts.** The solid superacid catalysts  $ZrO_2/SO_4$  and Pt-stabilized  $ZrO_2/SO_4$  (0.5%Pt), were prepared by Wender and Shabtai as described in previous papers[2,5]. The zeolite-based HZSM-5 catalyst was supplied by Aldrich Chemical Co.

**Experimental Procedure.** Experiments with high density polyethylene (HDPE) and HDPE-rich waste plastic in the presence of various catalysts were performed in a high pressure TG/GC/MS system under different hydrogen pressures (or helium). Details of the high pressure TG/GC/MS system have been described previously[6]. Different temperature programs were employed to better distinguish the effect of different conditions on reaction kinetics.

Dry blending of catalyst and polymer was performed by hand mixing the powdered material inside a quartz TG crucible with a thin metal rod. To achieve better blending of catalyst and polymer, 30 mg polymer samples were dissolved in 10 ml of toluene at about 100 °C. After the addition of catalyst, the mixture was shaken while the solvent was removed and then dried for 3 hours at 130°C. Sample quantities of 30-40 mg were used in each TG/GC/MS experiment.

## Results and Discussion

### Catalyst loading and solvent blending

Figure 1a demonstrates that both a catalyst (here at 16% loading) and hydrogen atmosphere are

needed to achieve sustained high degradation rates at 375 °C. However increased hydrogen pressure above 600 psig does not produce markedly higher rates at this temperature. Figure 1b indicates that improved blending of polymer and catalyst using a solution slurry method in toluene can be as effective as increasing catalyst loadings. Interestingly, the first weight loss appears to occur just above 200 °C. As shown in Figure 1c, increasing the catalyst loading to 25% leads to complete decomposition of HDPE below 300 °C during the heat-up phase. Even a (much less reactive) waste plastic sample shows more than 40% weight loss before reaching the isothermal heating stage at 375 °C under these conditions. Therefore, it appears that physical (transport related) process are rate limiting in the case of HDPE polymer. If so, higher conversion rates and lower reaction temperatures should be achievable by measures that increase catalyst loadings and facilitate contact between the catalyst surface and the polymer matrix.

These observations encouraged us to go to much lower temperatures as well as higher catalyst loadings. Figure 2a shows that very fast degradation rates can be achieved at 200 °C and 600 psig H<sub>2</sub> when using pure HDPE and Pt stabilized ZrO<sub>2</sub>/SO<sub>4</sub> at 50 % loading whereas only minimal weight loss is observed when using solvent blending of 50% non Pt stabilized ZrO<sub>2</sub>/SO<sub>4</sub> or 50% HZSM-5. Clearly, HZSM-5 induced rates are not enhanced by the same factor as the superacid catalyst rates. Apparently, the rate limiting step is not affected by just increasing the amount of catalyst surface available. Possibly other factors such as diffusion into the HZSM-5 zeolite cavity may be rate limiting here, as also evident in figure 1a. Reduction of the H<sub>2</sub> pressure to 25 psig causes marked rate reduction. However, further increase of catalyst loading to 70% can largely enhance the reaction rate and yield as shown in figure 2b.

The reaction conditions illustrated in figure 2b are worth contemplating a little further, as they suggest that HDPE in more or less pure form can nearly be degraded in a household style pressure cooker (200 °C and 25 psig), thus potentially reducing the high cost of high temperature, (high) pressure reaction vessels, and auxiliary systems.

#### Temperature

Figure 3a and b illustrate the effect of temperature on the reaction rates of two different HDPE model compounds, obtained from HTI (MW: 250,000) and Aldrich (MW: 125,000) respectively. Note that the HDPE from HTI appears to be more reactive (in spite of its higher MW) both with regard to maximum rate achieved as well as highest conversion yield. The cause of the nearly 10% residue in the Aldrich sample at 200 °C is unknown. This is not simply char formation, since all of the residue is converted at 400 °C. Further studies are underway to explain this phenomenon.

#### Pressure of H<sub>2</sub>

Figure 4 a,b,c illustrate the effect of changes in H<sub>2</sub> pressure on the two different pure HDPEs and on a HDPE-rich waste plastic sample. The HTI sample degraded faster and more completely at 200 °C than the Aldrich sample. Furthermore, figure 4c illustrates that nearly 80% of the waste polymer sample can be converted at 200 °C.

#### Sorted waste plastic

The effects of contaminants, additives or residues on the conversion behavior of waste polymers are also well recognized. A variety of organic (e.g. sulfur or nitrogen containing) and inorganic (e.g. heavy metal containing) compounds are known to be capable of deactivating catalysts. Among the catalysts known to be effective in degrading polymethylenic bonds, the superacids are known to be highly susceptible to activity loss through coke deposit formation. Figure 5 shows the behaviour of a variety of waste plastic samples indicating wide differences in the reactivity of the specific waste plastic components which were hand-picked from the APC sample, e.g. clear (HDPE rich) materials, white (filled) cap components and labels (or label like) material. Individual component profiles and mixture profiles are shown in figure 5. Note how the clean milk bottle sample degraded as fast as pure HDPE model compound. "Cap material" behaves much like a moderately char forming polymer. Note that the initial 30% residue formed at 200 °C nearly completely degrades at approx. 450 °C, thus reducing the likelihood that an inorganic filler is responsible for the observed residue. Finally, the paper/label like fraction (handpicked) does not show any detectable weight loss below 300 °C. The mixture samples of "paper" + "plastic" and "paper" + "cap" + "plastic" show marked residue formation. The fact that the measured conversion rates and yields fall well behind the predicted rates of summed weight loss curves of the components suggest the effects of catalytic deactivation.

By examining the evolution profiles of volatile products by means of GC/MS, the distribution of

different types of product distributions as a function of reaction gas and catalysts can be measured. Figure 6 shows that effective catalysts increase the degree of saturation and markedly decrease the degree of aromaticity (nearly zero) in addition to increasing reaction rates and decreasing reaction temperature as shown in Figure 1. HZSM-5 also showed a tendency to promote the formation of aromatic products (not shown here) as noted in previous experiments[7]. In addition, the product distributions of thermal reaction in  $H_2$  or He are different, although their reaction rates are nearly the same as shown in Figure 1a. Typical analytical results corresponding to curve 3 in Figure 2a are demonstrated in Figure 7. The repetitive chromatogram for the whole run (Figure 7a) indicates that the catalytic decomposition of HDPE occurs in the about 16–35 minutes run time (200 °C isothermal). Furthermore, by selecting a particular ion chromatogram, the evolution ratio of the corresponding products during the reaction can be visualized. The expanded total ion chromatogram for one sampling interval (Figure 7b) shows the range of GC separated paraffin products which are similar to the products for non Pt promoted  $ZrO_2/SO_4^{2-}$ [7]. The predominance of saturated aliphatic products is shown in the 15 to 37 minute average mass spectrum (7c).

## Conclusions

Platinum stabilized  $ZrO_2/SO_4^{2-}$  ( $Pt/ZrO_2/SO_4^{2-}$ ) is much more effective than non promoted  $ZrO_2/SO_4^{2-}$  in maintaining high conversion rates for HDPE polymers and HDPE-rich waste plastic at 200°C. Also, it readily outperforms HZSM-5. Even under low pressure (25 psig  $H_2$ ) conditions,  $Pt/ZrO_2/SO_4^{2-}$  shows high activity by means of high catalyst loading and solvent blending. In addition, there are wide differences in the reactivity of the various waste plastic components over  $Pt/ZrO_2/SO_4^{2-}$ . Furthermore, the on-line GC/MS monitoring technique offers an effective tool in studying catalytic conversion processes.

## References

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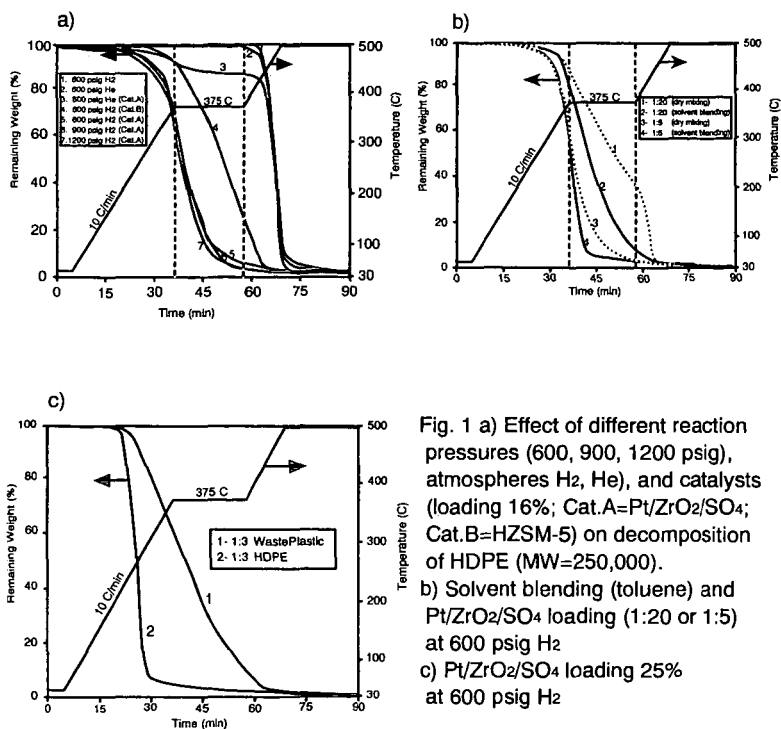


Fig. 1 a) Effect of different reaction pressures (600, 900, 1200 psig), atmospheres H<sub>2</sub>, He), and catalysts (loading 16%; Cat.A=Pt/ZrO<sub>2</sub>/SO<sub>4</sub>; Cat.B=HZSM-5) on decomposition of HDPE (MW=250,000).  
 b) Solvent blending (toluene) and Pt/ZrO<sub>2</sub>/SO<sub>4</sub> loading (1:20 or 1:5) at 600 psig H<sub>2</sub>  
 c) Pt/ZrO<sub>2</sub>/SO<sub>4</sub> loading 25% at 600 psig H<sub>2</sub>

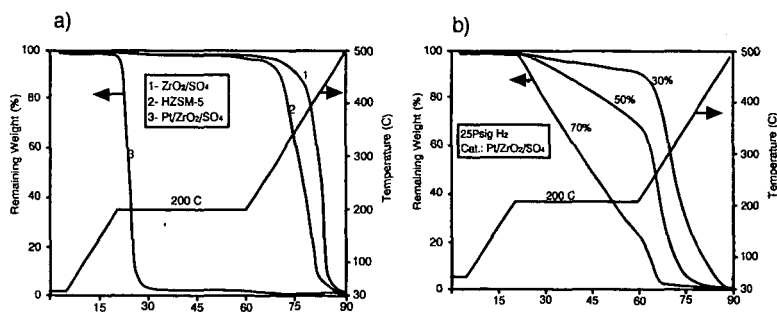


Fig. 2 a) Effect of different catalysts at 50% loading at 600 psig H<sub>2</sub>.  
 b) Effect of different catalyst loadings at 25 psig H<sub>2</sub>.

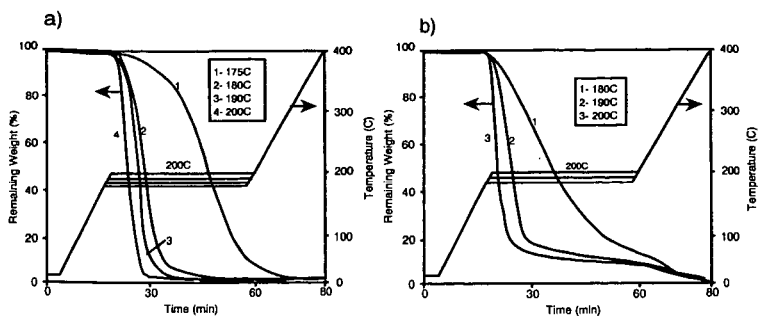


Fig. 3 Effect of temperature on degradation of different HDPEs at 600 psig  $H_2$  with  $Pt/ZrO_2/SO_4$  loading 50%  
 a) HTI HDPE(MW=250,000), b) Aldrich HDPE(MW=125,000)

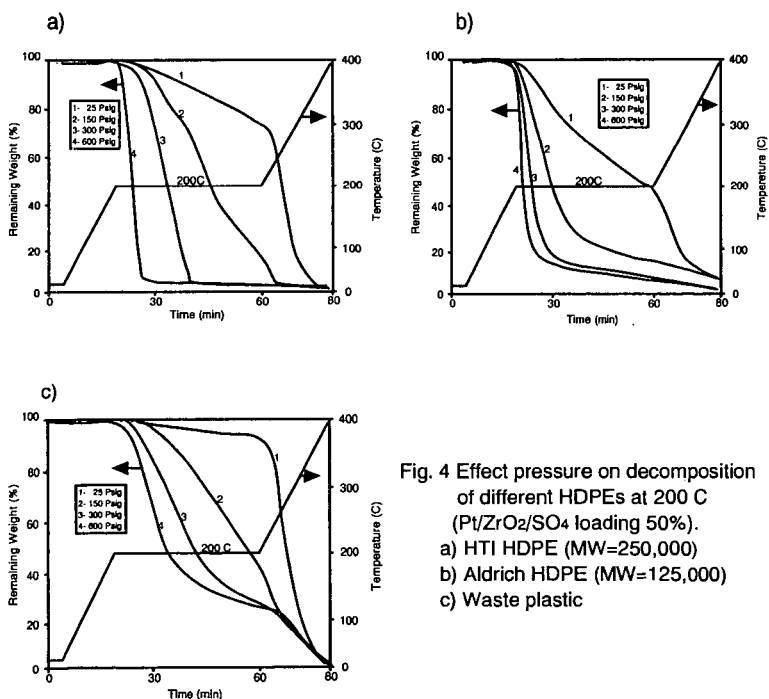


Fig. 4 Effect pressure on decomposition of different HDPEs at 200 C ( $Pt/ZrO_2/SO_4$  loading 50%).  
 a) HTI HDPE (MW=250,000)  
 b) Aldrich HDPE (MW=125,000)  
 c) Waste plastic

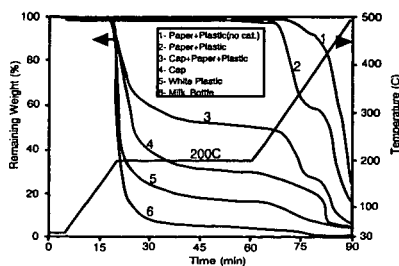


Fig. 5 TG profiles for decomposition of components of waste plastic at Pt/ZrO<sub>2</sub>/SO<sub>4</sub> loading 50% (except 1)

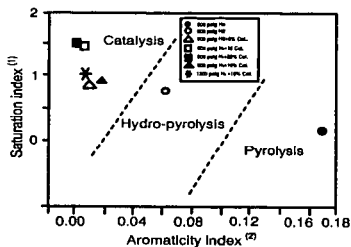


Fig. 6 Comparison of evolution product's saturation and aromaticity with different Pt/ZrO<sub>2</sub>/SO<sub>4</sub> catalyst loadings and pressures  
(1)  $(m/z77+m/z91)/(m/z43+m/z57)$   
(2)  $(m/z43+m/z57)/(m/z41+m/z55)$

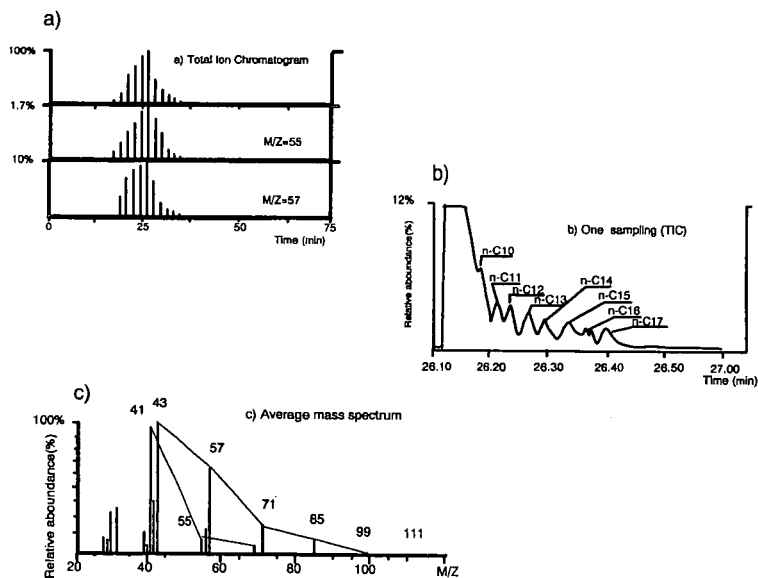


Fig. 7 GC/MS analysis corresponding to Curve 3 in Fig. 2a.

- Total ion chromatogram.
- Total ion chromatogram for one sampling interval.
- Average mass spectrum from 15 to 37 minute from 7a.